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COMPLETE SPECIFICATION

Improvements in or relating to Luminescent Materials

- We, THE GENERAL ELECTRIC COMPANY LIMITED, of 1 Stanhope Gate, London, W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to luminescent materials of the kind consisting of crystalline inorganic material activated so as to be excitable to luminescence by one or more of the usual exciting agencies, namely ultra violet radiation of long wavelength, that is to say of wavelength greater than 3000 Å, ultra violet radiation of short wavelength, that is to say of wavelength less than 3000 Å, cathode rays and X-rays.
- It is an object of the invention to provide a luminescent material of the kind referred to, of novel composition and having useful luminescent properties, and a method of manufacturing such material. The invention also includes within its scope electrical devices, such as high pressure and low pressure mercury vapour fluorescent electric discharge lamps, cathode ray tubes, and X-ray screens, which incorporate a luminescent material in accordance with the invention, the luminescent material being so disposed and the device so arranged that the material is excited to luminescence during operation of the device.
- Luminescent materials which are composed of a matrix of an alkaline earth metal silicate, activated by europium, have been described in our earlier Patent Specification No. 544,160, these materials preferably being produced by heating a mixture of the alkaline earth metal oxide or carbonate, silica, and a europium compound, and the proportion of europium incorporated therein being about 0.1% of this mixture by weight. We have now found that by the inclusion of a compound of fluorine or chlorine in a starting mixture containing an alkaline earth metal compound and silica, and at the same time incorporating a higher proportion of europium in the mixture, it is possible to produce luminescent materials of novel composition and crystal structure and having different luminescent properties from those of the materials described in the aforesaid specification.
- Thus according to one aspect of the present invention, a luminescent material is composed of the elements silicon, oxygen, one or more of the alkaline earth metals, one or both of the halogens fluorine and chlorine, and europium in the divalent state, the proportion of europium being in the range of 0.5% to 20% by weight of the material, and the material being activated by the europium present so as to be excitable to luminescence by ultra violet radiation of wavelength 2537 Å and of wavelength 3650 Å, and by cathode rays.
- It is to be understood that the term "alkaline earth metals" as used in the present specification includes only the metals calcium, strontium and barium. The preferred alkaline earth metal is strontium and the preferred halogen is chlorine: thus the materials in accordance with the invention which possess the most advantageous luminescent properties are those containing strontium and chlorine, which materials will be referred to hereinafter, for convenience, as strontium chlorosilicates. The luminescent materials of the invention, in general, will similarly be referred to as alkaline earth metal halosilicates.
- According to another aspect of the invention, a method of manufacturing a luminescent material includes the steps of forming an intimate mixture of compounds containing the elements silicon, oxygen, one or more of the alkaline earth metals, one or both of the halogens fluorine and chlorine, and europium, and heating the mixture in a reducing atmosphere at a temperature in the range of 825° C to 975° C, the starting mixture of

M 20

compounds being such that the product of the heating consists only of the said elements and contains a proportion of europium in the range of 0.5% to 20% by weight.

5 Silicon is usually included in the starting mixture in the form of the oxide, SiO_2 ; the, or each, alkaline earth metal may be introduced as the oxide or a compound decomposed to form the oxide during the heating, 10 such as the carbonate, and/or as the appropriate halide; and the, or each, halogen, if not incorporated as the alkaline earth metal halide, may be introduced as the ammonium halide or, in the case of chlorine, as hydrochloric acid. The europium may be introduced as the oxide or a decomposable compound such as the carbonate, in powder form 15 intimately mixed with the other ingredients of the mixture; preferably, however, especially when the europium is required only in small quantities, an aqueous solution of a water-soluble europium salt, such as the nitrate, is mixed with the solid ingredients to form a paste. Thus examples of suitable 20 starting mixtures include the following, in each case in suitable relative proportions as will be described below, and with a solution of europium nitrate or other suitable europium compound: an alkaline earth metal fluoride 30 or chloride and silica; an alkaline earth metal carbonate, silica, and ammonium fluoride or ammonium chloride; an alkaline earth metal carbonate, an alkaline earth metal fluoride or chloride, and silica; an alkaline earth metal 35 oxide, silica, and ammonium chloride or hydrochloric acid or ammonium fluoride. If desired europium chloride may be employed as the source of europium and part of the chlorine.

40 The reducing atmosphere employed for the heating step preferably consists of hydrogen, although a mixture of hydrogen and nitrogen can alternatively be used. The preferred temperatures are in the range of 890°C to 920°C . In some cases a second heating, carried 45 out under the same conditions as the first heating, is advantageous in enhancing the luminescent properties of the product. The

duration of the, or each, heating step is suitably half to one hour.

The luminescent materials of the invention are excited by ultra violet radiation of both wavelengths 2537 \AA and 3650 \AA to exhibit luminescence of a blue or pink or violet colour, 55 the colour and intensity depending upon the alkaline earth metal and halogen present: thus the materials containing strontium and chlorine exhibit luminescence varying from a bright deep blue to a bright blue-green, and the luminescence of materials containing calcium or barium, or fluorine as the only halogen, is violet in colour and less bright than 60 that of the strontium chlorosilicates. The materials are also excited by cathode rays and X-rays, and in some cases also by the electric discharge in neon, in each case giving luminescence of a similar colour to that shown under ultra violet excitation. The europium-activated strontium chlorosilicates possess 65 satisfactory temperature characteristics, the brightness of the luminescence decreasing only very slightly up to a temperature of 300°C and a little more rapidly above this temperature, but luminescence being still apparent up to about 500°C .

Examination of europium-activated strontium chlorosilicate luminescent materials in accordance with the invention by X-ray crystal analysis techniques has shown that 80 these materials consist of or include a substance which possesses a novel crystal structure and which apparently is responsible for the blue luminescent characteristic of these materials: chemical evidence indicates that 85 this substance contains chlorine. The interplanar spacings and relative intensities of the first 29 X-ray reflections have been determined, for the said substance of novel structure, by examination of this substance by the method of X-ray analysis set out in the pamphlet designated by No. E.43-49T, 90 issued by the American Society for Testing Materials in 1942 and revised in 1946 and 1949: the spacings (d/n) of these reflection lines, as measured in Angstrom units, and their relative intensities (I/I_1) as estimated 95 visually, are set out in the following Table.

TABLE

Line	d/n (Å)	I/I ₁
1	7.9	20
2	7.26	10
3	6.92	10
4	5.59	40
5	4.76	80
6	4.07	20
7	3.95	60
8	3.54	70
9	3.46	20
10	3.21	10
11	3.05	30
12	2.838	100
13	2.797	20
14	2.675	50
15	2.601	20
16	2.497	90
17	2.408	50
18	2.375	50
19	2.214	80
20	2.059	40
21	2.037	20
22	1.974	60
23	1.914	50
24	1.861	50
25	1.827	20
26	1.805	10
27	1.779	80
28	1.734	30
29	1.723	30

The chlorine-containing substance having the novel crystal structure as aforesaid is produced, as a result of the heating step, in the form of needle-shaped crystals. This substance, which is formed, during the heating, by the combination of chlorine with at least part of the strontium, silicon and oxygen derived from the starting mixture, may in some cases constitute the whole of the strontium chlorosilicate luminescent material, but is usually present as a phase in admixture with one or more other phases mainly consisting of strontium silicates and/or strontium chloride. The relative proportions of the said novel chlorine-containing phase and the other phase or phases, and the composition of the said phases or phases, may vary considerably, and will depend mainly upon the composition of the starting mixture employed for the manufacture of the material.

The chlorine content of the starting mixture employed for the manufacture of the strontium chlorosilicate luminescent materials does not appear to be critical, since even relatively small proportions of chlorine have a marked effect on the crystal structure of the product and give rise to the characteristic blue or blue-green luminescence. Preferably however, the chlorine content is sufficient to ensure that the novel chlorine-containing substance described above will be formed as the predominant phase in the luminescent material, and we have found that the brightest luminescence is obtained with materials produced from starting mixtures in which the atomic ratio of strontium to chlorine lies in the range of 1:2 to 1:1. We have also found that the emission spectrum of the strontium chlorosilicate luminescent materials tends to shift from the blue towards green with decreasing chlorine content, and that part of the chlorine initially included in the starting mixture tends to be lost during the heating of the mixture in the production of the luminescent materials; hence if it is desired to obtain a product having good blue emission, prolonged heating should be avoided; but in some cases sufficient heating to give a product showing a blue-green luminescence may be desirable, since the blue-green emission is particularly bright. A total heating time of 1 to 2 hours is usually suitable for ensuring the reaction of the starting mixture to form the aforesaid blue-luminescing substance in a predominant proportion, while avoiding the loss of a significant amount of chlorine.

The relative proportions of alkaline earth metal compound or compounds and silica in the starting mixture employed for the manufacture of the luminescent materials of the invention may vary within fairly wide limits, but preferably are such that the ratio of alkaline earth metal atoms to silica molecules is in the range of 2:1 to 1:2. Thus the luminescent materials may be regarded as

alkaline earth metal halosilicates of compositions corresponding to the orthosilicates and higher silicates, up to a molecular ratio $MO:SiO_2$ (where M is alkaline earth metal) of 1:2, wherein part of the oxygen is replaced by chlorine and/or fluorine.

It will be understood that the alkaline earth metal content of the luminescent materials in accordance with the invention may consist entirely of one of the metals calcium, strontium or barium, or may consist of any two or all of these metals in any proportions.

The europium compound included in the starting mixture may contain europium in either the divalent or trivalent state: in either case, as a result of the use of a reducing atmosphere for the heating step, the europium will be incorporated in the final product in the europous, or divalent, state. The preferred proportions of europium are in the range of 1% to 5% by weight of the product, for obtaining the optimum luminescent properties, the brightest emission in general being obtained from materials containing 2% by weight of europium.

The strontium chlorosilicate luminescent materials of the invention are especially advantageous for use in high pressure mercury vapour fluorescent electric discharge lamps, since they are strongly excited by ultra violet radiation of wavelength 3650 Å, and in view of the stability of the luminescence, under such excitation, up to the operating temperatures of such lamps. However, these materials, and the materials containing calcium, barium, and fluorine in place of or in addition to strontium and chlorine, are also suitable for use in low pressure mercury vapour fluorescent electric discharge lamps, cathode ray tubes, X-ray screens and, in some cases, neon discharge lamps.

It will be understood that the starting materials used in the manufacture of luminescent materials in accordance with the invention must be of a high degree of purity, as is usual in the preparation of luminescent materials.

Some specific methods which we have employed for the preparation of luminescent materials in accordance with the invention will now be described in the following Examples. The silica employed in all the preparations described is a bulky form of silica containing 15% by weight of water but otherwise free from impurity, specially prepared for the manufacture of luminescent materials and sold under the Registered Trade Mark "Mallinckrodt": the weights given in the Examples refer to this hydrated silica, and the molar proportions given refer to anhydrous silica, calculated from the quantities of "Mallinckrodt" silica used.

EXAMPLE 1

7.08 grams of hydrated strontium chloride, $SrCl_2 \cdot 6H_2O$, and 0.94 grams of silica,

$\text{SiO}_2 + 15\% \text{H}_2\text{O}$, were mixed together with sufficient water to form a thin paste, these weights of the ingredients corresponding to the molar proportions $2\text{SrCl}_2 \cdot 6\text{H}_2\text{O} : 1\text{SiO}_2$.

- 5 Europium was added to the paste in the form of a 2% (weight/volume) solution of europium nitrate in water, the amount of this solution mixed with the paste being sufficient to provide 0.1 gram of europium. The resulting slurry, after thorough stirring, was placed in an oven and dried overnight at a temperature in the range of 160°C to 250°C . The dried mixture was then ground to a powder fine enough to pass completely through a sieve having 150 meshes to the linear inch.

- 15 The sieved powder was loaded into a semi-cylindrical silica boat, which was placed in a silica tube closed at one end and plugged at the other end with a plug of glass wool through which a narrow glass tube was inserted. A mixture of nitrogen and hydrogen, the nitrogen flowing at the rate of 600 ccs per minute and the hydrogen at 30 ccs per minute, was passed through the glass tube and over the powder for a few minutes, then the nitrogen supply was switched off and the silica tube containing the powder was

placed in a furnace and heated at 910°C for one hour while the hydrogen flow was maintained at 30 ccs/min. Nitrogen was then admitted to the tube at the same rate as before, for a few minutes, and the silica tube was removed from the furnace and allowed to cool in the nitrogen-hydrogen atmosphere for 45 minutes. The product was then removed from the boat and ground lightly.

The product of the heating was a soft, very pale green material, readily ground to powder which consisted predominantly of needle-shaped crystals. This powder, which contained 2% by weight of europium, was strongly excited by ultra violet radiation of wavelengths 2537 \AA and 3650 \AA and by cathode rays and X-rays, to give a blue luminescence which diminished only very slightly in brightness when the powder was heated to 300°C .

In the following Examples 2 to 8, only the weights and molar proportions of the ingredients of the starting mixture used are stated: in each case the luminescent material was prepared by the same procedure as that described in Example 1, and the europium content of the final product was 2% by weight.

EXAMPLE 2

Weights of starting materials:—

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$:	6.14 grams
$\text{SiO}_2 + 15\% \text{H}_2\text{O}$:	1.62 grams
europium:	0.1 gram, in europium nitrate.

- 60 Molar proportions:— $1\text{SrCl}_2 \cdot 6\text{H}_2\text{O} : 1\text{SiO}_2$.

EXAMPLE 3

Weights of starting materials:—

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$:	4.80 grams
$\text{SiO}_2 + 15\% \text{H}_2\text{O}$:	2.53 grams
europium:	0.1 gram, in europium nitrate.

- 65 Molar proportions:— $1\text{SrCl}_2 \cdot 6\text{H}_2\text{O} : 2\text{SiO}_2$.

EXAMPLE 4

Weights of starting materials:—

Strontium carbonate, SrCO_3 :	3.92 grams
Ammonium chloride, NH_4Cl :	2.84 grams
$\text{SiO}_2 + 15\% \text{H}_2\text{O}$:	0.94 gram
europium:	0.1 gram, in europium nitrate.

- 70 Molar proportions:— $2\text{SrCO}_3 : 4\text{NH}_4\text{Cl} : 1\text{SiO}_2$.

EXAMPLE 5

- 75 Weights of starting materials:—

SrCO_3 :	3.92 grams
NH_4Cl :	1.5 grams
$\text{SiO}_2 + 15\% \text{H}_2\text{O}$:	0.94 gram
europium:	0.1 gram, in europium nitrate.

- 80 Molar proportions:— $2\text{SrCO}_3 : 2.1\text{NH}_4\text{Cl} : 1\text{SiO}_2$.

EXAMPLE 6

Weights of starting materials:—

	Calcium chloride, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$:	7.76 grams
	$\text{SiO}_2 + 15\% \text{H}_2\text{O}$:	1.25 grams
5	Europium:	0.1 gram, in europium nitrate.
	Molar proportions:— $2\text{CaCl}_2 \cdot 6\text{H}_2\text{O} : 1\text{SiO}_2$.	

EXAMPLE 7

Weights of the starting materials:—

	Barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$:	5.13 grams
10	$\text{SiO}_2 + 15\% \text{H}_2\text{O}$:	0.74 gram
	europium:	0.1 gram, in europium nitrate.
	Molar proportions:— $2\text{BaCl}_2 \cdot 2\text{H}_2\text{O} : 1\text{SiO}_2$.	

EXAMPLE 8

Weights of starting materials:—

15	SrCO_3 :	3.92 grams
	Ammonium fluoride, NH_4F :	0.49 gram
	$\text{SiO}_2 + 15\% \text{H}_2\text{O}$:	0.94 gram
	europium:	0.1 gram, in europium nitrate.
	Molar proportions:— $2\text{SrCO}_3 : 1\text{NH}_4\text{F} : 1\text{SiO}_2$.	

20 The products obtained from the starting materials specified in Examples 2 to 5 were all similar, in appearance and luminescent properties, to the product of Example 1. The product of Example 6 showed a moderate pink luminescence, and the products of Examples 7 and 8 a weak violet luminescence, in each case under excitation by ultra violet radiation of wavelengths 2537 Å and 3650 Å.

30 All of the strontium chlorosilicate materials produced in accordance with Examples 1 to 5 were found, on examination by X-ray analysis, to include a predominant phase of novel crystal structure identified by the interplanar spacings listed in the Table, above.

WHAT WE CLAIM IS:—

1. A luminescent material composed of the elements silicon, oxygen, one or more of the alkaline earth metals, as hereinbefore defined, one or both of the halogens fluorine and chlorine, and europium in the divalent state, the proportion of europium being in the range of 0.5% to 20% by weight of material, and the material being activated by the europium present so as to be excitable to luminescence by ultra violet radiation of wavelength 2537 Å and of wavelength 3650 Å, and by cathode rays.

2. A luminescent material according to Claim 1, wherein the alkaline earth metal constituent consists of strontium only.

3. A luminescent material according to Claim 1 or 2, wherein the halogen constituent consists of chlorine only.

4. A luminescent material according to Claim 1, which includes a substance composed of strontium, silicon, oxygen and chlorine and activated by the europium present

to be excitable to blue luminescence by the said ultra violet radiations and by cathode rays, which substance is in the form of needle-shaped crystals, and is identified by X-ray reflection lines having the interplanar spacings and relative intensities listed in the foregoing Table.

5. A luminescent material according to any preceding Claim, wherein the proportion of europium is in the range of 1% to 5% by weight of the material.

6. A luminescent material according to Claim 5, wherein the proportion of europium is 2% by weight of the material.

7. A method of manufacturing a luminescent material according to any preceding Claim, which includes the steps of forming an intimate mixture of compounds containing the elements silicon, oxygen, one or more of the alkaline earth metals, as hereinbefore defined, one or both of the halogens fluorine and chlorine, and europium, and heating the mixture in a reducing atmosphere at a temperature in the range of 825° C to 975° C, the starting mixture of compounds being such that the product of the heating consists only of the said elements and contains a proportion of europium in the range of 0.5% to 20% by weight.

8. A method according to Claim 7, wherein silicon is included in the said starting mixture in the form of silica; the, or each, alkaline earth metal is included in the form of the oxide, or of a compound decomposable during the heating to form the oxide, and/or of the fluoride and/or chloride; the halogen is included in the form of the alkaline earth metal fluoride and/or chloride, or of ammonium fluoride and/or chloride, or of hydrochloric acid; and europium is included in the form

of the oxide, or of a compound decomposable during the heating to form the oxide.

5 9. A method according to Claim 8, wherein europium is included in the said starting mixture in the form of an aqueous solution of europium nitrate.

10 10. A method according to Claim 7, 8, or 9, wherein the alkaline earth metal and halogen included in the said starting mixture consist of strontium and chlorine respectively, and the atomic ratio of strontium to chlorine in the starting mixture lies in the range of 1:2 to 1:1.

15 11. A method according to any one of the preceding Claims 7 to 10, wherein the relative proportions of alkaline earth metal compound or compounds and silica included in the said starting mixture are such that the ratio of alkaline earth metal atoms to silica molecules is in the range of 2:1 to 1:2.

20 12. A method according to any one of the preceding Claim 7 to 11, wherein the heating is carried out at a temperature in the range of 890° C to 920° C.

25 13. A method according to any one of the preceding Claims 7 to 12, wherein a second heating is carried out under the same conditions as the first heating step.

30 14. A method according to any one of the preceding Claims 7 to 13, wherein the duration of the, or each, heating step is half to one hour.

35 15. A method of manufacturing a luminescent material composed of the elements silicon, oxygen, one of the alkaline earth metals, as hereinbefore defined, one of

the halogens fluorine and chlorine, and europium in the divalent state, which method is carried out substantially as hereinbefore described in any one of the specific Examples. 40

16. A luminescent material which has been manufactured by a method according to claim 15.

17. An electrical device incorporating a luminescent material according to any one of the preceding Claims 1 to 6 and 16, the said material being so disposed and the device so arranged that the material is excited to luminescence during operation of the device. 45

18. A high pressure mercury vapour electric discharge lamp incorporating a luminescent material according to any one of the preceding Claims 1 to 6 and 16, the said material being so disposed as to be excited to luminescence by the discharge passing through the lamp in operation thereof. 50

19. A low pressure mercury vapour electric discharge lamp incorporating a luminescent material according to any one of the preceding Claims 1 to 6 and 16, the said material being so disposed as to be excited to luminescence by the discharge passing through the lamp in operation thereof. 55

20. A cathode ray tube incorporating a luminescent material according to any one of the preceding Claims 1 to 6 and 16, the said material being so disposed as to be excited to luminescence by the cathode rays generated in the said tube in operation thereof. 60

For the Applicants,
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